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NMR AND MODULATED DIFFERNETIAL SCANNING CALORIMETERY OF ADSORBED PMA ON SILICA

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Introduction

The interaction between polymers and solid substrates can be studied by a variety of techniques. The results from different experiments can be affected by the nature of the polymer, surface, polymer-surface interactions and, also, the experiment. A great deal has been learned about the behavior of polymers at interfaces, but there is also much to be learned about the interactions and how they affect the physical properties of adsorbed polymers.

In the present study, we report both deuterium nuclear magnetic resonance (NMR) and modulated differential scanning calorimetry (MDSC) of poly(methyl acrylate) (PMA) adsorbed on Cab-O-Sil silica. The focus of this study is on the dynamics of polymer segments and the interfacial glass transition temperature (T_g). In our case, very small amounts of polymer were adsorbed, and we can view behavior of polymer segments in close proximity to the silica surface. We found that both NMR and MDSC experiments provide consistent insight into the dynamics of adsorbed polymers. Both experiments show the heterogeneous nature of the adsorbed polymers, with the polymer segments closer to the solid surface being the most motionally restricted resulting in a higher T_g for those segments.

Experimental

Methyl acrylate-d3, was synthesized using methanol-d4 (CIL), acryloyl chloride, triethylamine, and toluene. The synthesis of poly(methyl acrylate)-d_3 (PMA) was performed by atom transfer radical polymerization (ATRP). More details of the synthesis are given elsewhere.[1] The molecular masses of the polymer samples were measured using an OPTILAB DSP Interferometer Refractometer and a DAWN EOS Light Scattering Instrument (Wyatt Technology, Santa Barbara), connected to a gel permeation instrument. The molecular masses of the polymers varied from about 5000 to 165000 g/mol and had relatively low polydispersities. The substrate used was Cab-O-Sil silica which consists of congealed balls of non-porous amorphous silica, Grade M-5 (surface area 200 m^2/g).

Solutions of PMA in toluene were mixed with silica, placed on a mechanical shaker for 48 h, and then centrifuged for an hour. The supernatant liquid was decanted and the solid-containing portion was kept in a vacuum oven for 36 h. Thermogravimetric analysis (TA Instruments Model 2950 TGA) was used to estimate the adsorbed amounts of polymer on the silica.

Deuterium NMR experiments were performed on a Varian VXR-200/S spectrometer operating at 61.4 MHz for deuterium. The quadrupole-echo pulse sequence (delay-90°$_y$-□-90°$_x$-□-acquisition) was used with about a 2.7 □s 90° pulse width with an echo time of 30 µs. For the bulk and adsorbed samples, 256 scans and 4096 to 8192 scans were used, respectively. A line broadening of 1 kHz was applied for the adsorbed sample data set. The MDSC experiments were performed using a TA Instruments Model 2920 MDSC. The traces reported were shown in derivative mode from the second heating cycle (used to ensure similar thermal histories for the different samples). The thermograms were typically taken in a range of –40 to 60 °C, with a heating rate of 5 °C/min, and a modulation amplitude of ± 1°C and period of 1 min.

Results and Discussion

Shown in **Figure 1A** are representative deuterium NMR spectra of PMA-d_3, in bulk, as a function of molecular mass. These spectra were selected because at 35 °C they clearly show the differences between the different molecular mass samples in the NMR glass transition region. The 165k and 77k samples had their segments in the rigid regime. The spectra show a Pake-powder pattern for these samples. The 38k sample was just below its T_g(NMR) and the 5k sample was clearly above its T_g as evidenced by the narrow resonance. More detailed information on the temperature dependence of these samples is given in prior work.[1,2]

The ^{2}H NMR spectra of the same samples adsorbed on silica are shown in **Figure 1B**. At 55 °C, the spectra for the surface adsorbed samples showed that each sample was *heterogeneous* with respect to segmental dynamics. Each sample showed some amount residual powder pattern in addition to a narrow component in the middle of the spectrum. Interestingly, the relative amount of material corresponding to the motionally narrowed components was not monotonic with molecular mass. The sample with the lowest amount of mobile component was the 77k sample. This observation was consistent with earlier work on polydisperse PMA samples adsorbed on silica[3] where a roughly 1100k PMA surface-adsorbed sample had a higher fraction and faster motionally narrowed component than a 70k sample. One might surmise that there appears to be a complicated balance between the conformation of the polymer on the surface and the inherent mobility of the polymer segments.

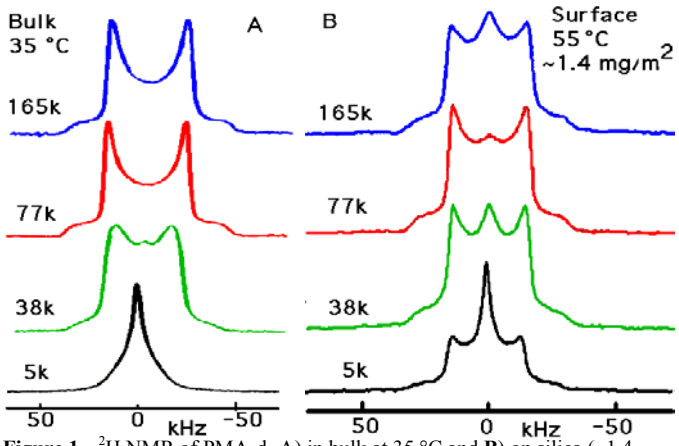

Figure 1. ^{2}H NMR of PMA-d_3 A) in bulk at 35 °C and **B**) on silica (~1.4 mg/m^2) at 55 °C for different molecular mass samples.

In **Figure 2**, the MDSC scans are shown for the different molecular mass samples that were studied with NMR. It can be seen from the figure that the T_g of the bulk polymers (the top point in the derivative curve) increases with molecular mass, leveling out at the two highest molecular masses. For all of the samples, the glass transition range was much broader for the adsorbed samples than the bulk ones. The contrast between the MDSC results for the bulk and adsorbed PMA was consistent with the notion from the NMR data that the bulk polymer segments behaved in a more homogeneous manner compared to the surface samples which were much more heterogeneous. Interestingly, while it is a small effect, the thermal transition for the 77k adsorbed sample has the highest temperature for the peak in the derivative curve. This is also consistent with the NMR data which show that this sample (77k) has the smallest amount of mobile component.

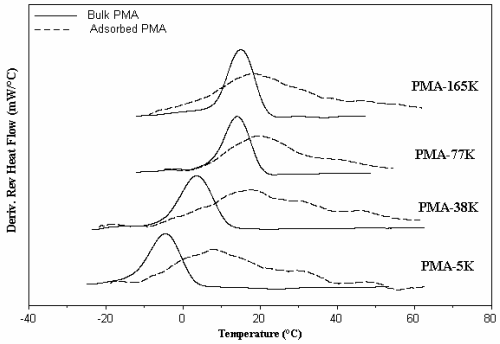

Figure 2. MDSC for different molecular mass samples of PMA in bulk (solid curves) and on silica (dashed curves, ~1.4 mg/m^2).

Conclusions

NMR and MDSC have been shown to be in excellent qualitative agreement with respect to the behavior of adsorbed PMA on silica. Differences in the T_gs measured by the two different experiments were consistent with the differences in the time scales of the two experiments. Both experiments are consistent with the notion that the bulk polymer dynamics is relatively *homogeneous* while that for the adsorbed polymers is *heterogeneous*. The dependence of the dynamics and MDSC transitions on molecular mass suggests that there is a molecular mass for which the surface polymer has the minimum mobility. For PMA on silica this appears to be on the order of 80k (more or less).

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References

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